

## TECHNICAL PAPER

# Mass transfer inside membranes, explained

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Version 1.0

### Abstract

The principle of membrane distillation is easy to explain and to understand. It describes a natural process of evaporation and condensation over a hydrophobic membrane. However the mathematical description of this process used for quantifying mass -and heat transfer can be very useful for the optimization of membrane distillation modules. Another purpose is the use of modelling for prediction of CAPEX and OPEX costs. These costs are mainly determined by flux and energy performance of the process. Aquastill describes in a set of technical papers the different aspects of the MD process to give a deeper understanding in this complex matter. This article describes the second step in a series of sub-processes in heat transfer inside modules which describes the calculation of the mass transfer inside membranes (F).

### Solution

Mass or heat transfer generally needs a driving force such as a temperature difference (heat exchangers), pressure differences (filtration), concentration differences (diffusion) etc. These driving forces often must overcome a material forming the barrier between the two mediums. The driving force together with the resistance of the barrier (membrane permeability) determines the flux (amount of mass or heat transferred per area per time slot).

### General formula for mass transfer inside membranes

The driving force in membrane distillation is the pressure difference which is caused by the temperature difference over the membrane. The formula to calculate the flux of the distillate is based

on a pressure difference is described with Darcy's law (Martinez & Rodriguez-Maroto, 2006, 2007):

$$F = C_m(p_1 - p_2) \cdot 3600 \text{ [kg/(m}^2\cdot\text{hr)]}$$

With:

F= flux [kg/(m<sup>2</sup>·hr)]  
 C<sub>m</sub>= membrane permeability [kg/(m<sup>2</sup>·s·Pa)]  
 p<sub>i</sub>= vapor pressure [Pa] (p<sub>1</sub>= brine side , p<sub>2</sub>= permeate side)

The vapor pressure close to the membrane surface isn't measurable so it's easier to rewrite Darcy's law with surface temperatures. Schofield, Fane, & Feil (1987) suggested to use the Clausius-Clapeyron relationship if temperature difference over the membrane is smaller than 10°C. In this case a mean average temperature can be used:

$$\left(\frac{dp}{dT}\right) = \left(\frac{p_{air} \cdot \Delta H_v}{R \cdot T_m^2}\right)$$

p<sub>air</sub>= vapor pressure inside membrane pores [Pa]  
 ΔH<sub>v</sub>= Evaporative heat [J/mol]  
 R= gas constant [J/(mol·K)]  
 T<sub>m</sub>= mean average temperature inside membrane pores [K]

Using this formula Darcy's law can be rewritten to:

$$F = C_m \cdot \left(\frac{p_{air} \cdot \Delta H_v}{R \cdot T_m^2}\right) \cdot (T_1 - T_2) \cdot 3600 \text{ [kg/(m}^2\cdot\text{hr)]}$$

With:

F= flux [kg/(m<sup>2</sup>·hr)]  
 C<sub>m</sub>= membrane permeability [kg/(m<sup>2</sup>·s·Pa)]  
 p<sub>air</sub>= average vapor pressure in membrane pores [Pa]  
 ΔH<sub>v</sub>= Evaporative heat [J/mol]  
 R= gas constant [J/(mol·K)]  
 T<sub>m</sub>= average temperature inside membrane pores [K]  
 T<sub>i</sub>= membrane surface temperature [K]  
 (T<sub>1</sub>=brine (warm), T<sub>2</sub>=permeate)

As said before the vapor pressure isn't measurable at the membrane surface but is also not measurable inside the membrane pores (p<sub>air</sub>). To calculate the vapor pressure inside the pores Antoine's law is used. This relationship between temperature and

vapor pressure is using the three so called Antoine constants. These constants differ for each medium and are only usable within a certain temperature range:

$$p_{air} = \exp\left(A - \frac{B}{C+T_{air}}\right) \text{ [Pa]}$$

With:

p<sub>air</sub>= average vapor pressure inside membrane pores [Pa]  
 T<sub>air</sub>= temperature inside membrane pores [K]  
 B and C= medium specific Antoine-coefficients [-]

Tabel 1: Antoine coefficients water

Medium	A	B	C	Tmin [°C]	Tmax [°C]
Water	23,238	3841,276	-45	1	100

### Membrane permeability

To calculate flux through the membrane three mechanisms inside the pores are responsible for mass transfer:

1. Viscous flow
2. Knudsen diffusion (D<sub>k</sub>)
3. Molecular diffusion (pD<sub>m</sub>)

The viscous flow is neglectable compared to the other two mechanism due to the low pressure difference over the membrane. (Schofield,1989; Lawson & Lloyd, 1996).

Knudsen diffusion is describing the process of water vapor molecules colliding with the wall surface inside pores. (Srisurichan, Jiraratananon, & Fane, 2006):

$$D_k = \frac{2r_p}{3} \sqrt{\frac{8RT_m}{\pi M_w}} \text{ [m}^2\text{/s]}$$

With:

D<sub>k</sub>= Knudsen diffusion [m<sup>2</sup>/s]  
 r<sub>p</sub>= radius of the pores [m]  
 R= gas constant [J/(mol·K)]  
 T<sub>m</sub>= average temperature inside membrane pores [K]  
 M<sub>w</sub>= molecular weight of water [kg/mol]

Molecular flow is describing the collision process between the water molecules themselves inside the pores:

$$\rho D_m = 4,46 \cdot 10^{-6} T_m^{2,334} \text{ [m}^2/\text{s]}$$

With:

$\rho D_m$  = molecular diffusion [m<sup>2</sup>/s]  
 $T_m$  = average temperature inside membrane pores [K]

The relevant equations for the transitional flow between Knudsen and molecular diffusion in the Dusty Gas Model are given by Field et al. [10], where the degree of Knudsen transport in the transitional region is weighted based on the Knudsen number. Both processes are existing next to each other and can be written by using the Dusty gas model (Schofield et. al. (1987), Mason & Malinauskas (1983), Martinez & Rodriguez-Maroto (2006) en Lawson & Lloyd (1996)):

$$C_m = \frac{\epsilon_m}{\tau_m \delta_m} \frac{M_w}{RT_m} \left( \frac{1}{D_k} + \frac{p_{air}}{\rho D_m} \right) \text{ [kg/(m}^2 \cdot \text{s} \cdot \text{Pa)}]$$

With:

$C_m$  = membrane permeability [kg/(m<sup>2</sup>·s·Pa)]  
 $\epsilon_m$  = membrane porosity [-]  
 $\tau_m$  = membrane tortuosity [-]  
 $\delta_m$  = membrane thickness [m]  
 $M_w$  = molecular weight water [kg/mol]  
 $R$  = gas constant [J/(mol·K)]  
 $T_m$  = average temperature inside membrane pore [K]  
 $D_k$  = Knudsen diffusion [m<sup>2</sup>/s]  
 $p_{air}$  = air pressure inside membrane pores [Pa]  
 $\rho D_m$  = molecular diffusion [m<sup>2</sup>/s]

A new unit is introduced called the membrane tortuosity. This tortuosity is the ratio between the realistic travel length of a water molecule through a membrane compared to the thickness of the membrane.

Figure 1 gives a more visual explanation (Srisurichan, Jiraratananon, & Fane, 2006):



Figuur 1: Cross-sections of porous membranes with different tortuosities (2004) door R.W. Baker

The tortuosity is depending on the porosity of the membrane and is described with the following relation:

$$\tau_m = \frac{(2 - \epsilon_m)^2}{\epsilon_m} \text{ [-]}$$

With:

$\tau_m$  = membrane tortuosity [-]  
 $\epsilon_m$  = membrane porosity [-]

The Dusty gas model given above can now be used to calculate the flux. Taken into account the pores can also be filled with an air fraction beside water vapor an additional correction (1-Y/Y) is needed because of the influence on the mass transport through the membrane.

Working with saline liquid means evaporation will be more difficult due to boiling point elevation. The largest fraction of salt in brine is usually sodium chloride. To correct for the influence of salt we use the so called activity coefficient ( $\alpha_c$ ). This leads to the following formula to calculate flux:

$$F = C_m \cdot p_{air} \frac{\Delta H_v}{RT_m^2} \Delta T|_{est} \left( \frac{1-Y}{Y} \right) \alpha_c \cdot 3600 \text{ [kg/(m}^2 \cdot \text{hr)}]$$

With:

$F$  = flux [kg/m<sup>2</sup>·hr]  
 $C_m$  = membrane permeability [kg/(m<sup>2</sup>·s·Pa)]  
 $p_{air}$  = air pressure membrane pores [Pa]  
 $\Delta H_v$  = evaporative heat of water [J/mol]  
 $R$  = gas constant [J/(mol·K)]  
 $T_m$  = average temperature inside membrane pores [K]  
 $\Delta T|_{est}$  = estimated temperature difference over the membrane for the calculation of mass transfer [K]  
 $Y$  = fraction of air inside the pore [-]  
 $\alpha_c$  = activity coefficient [-]

### Validation

By building a series of DCMD modules based on our MD design and leaving some materials out, a big dataset of measurements was generated for validation purposes.

As shown in the graph the predicted values according to the mathematical model are in alignment with the measured values indicating the model is useful for calculations of DCMD modules.

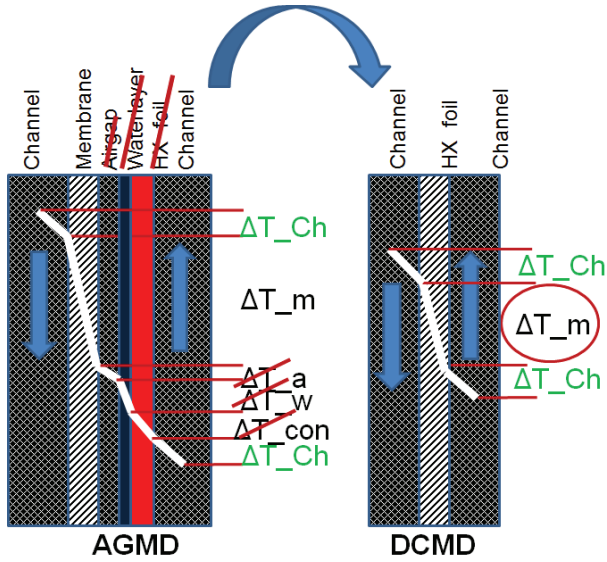


Figure 2: Schematical presentation of temperature profiles

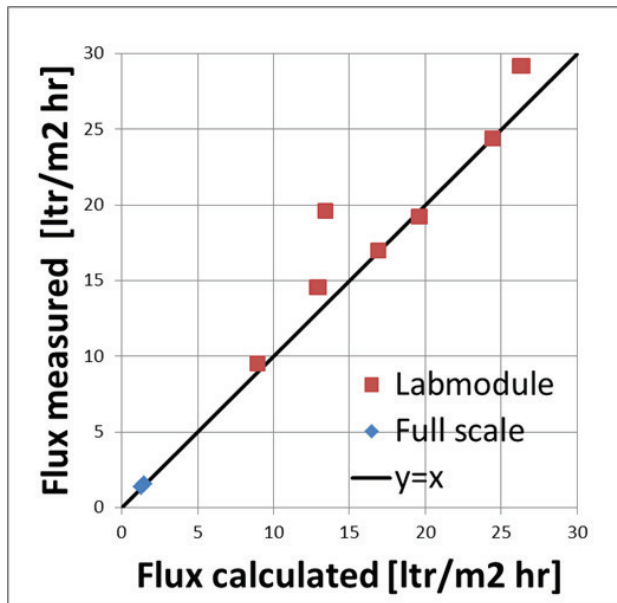


Figure 3: Validation of modeled fluxes with measured fluxes